SUPPLEMENTARY MATERIALS – MATERIALS AND METHODS

Reagents, standards, and materials

All reagents used in the study were analytically pure. Methanol (HPLC grade) and acetone (HPLC grade) were purchased from Chempur, Poland. Ethyl acetate (HPLC grade) and water (HPLC grade) were purchased from POCh, Poland. 1,2-propanodiol (99% extra pure) and ethylene glycol (99%, extra pure) were purchased from Acros Organics, USA. Acetonitrile (extra pure) and carbon disulfide (extra pure) were purchased from Merck, USA. Nitric acid 69-70% (pure for analysis) and 60% (ultrapure) were purchased from J.T. Baker, Holland, and Merck, Germany, respectively.

Chromatography standard mixture TO11/IP-6A (2,4-dinitrophenylhydrazine DNPH derivatives of carbonyl compounds in acetonitrile, 15 µg/mL each) was purchased from Sigma Aldrich, USA. Chromatography standard mixture EPA 8020/8040 (aromatic volatile organic compounds in methanol, 100 µg/ml each) and naphthalene standard in methanol (5000 µg/mL) were purchased from Supelco, USA. Multielemental and monoelemental standards were obtained from Merck, Germany. TSNAs and their isotopically labeled analogues were obtained from Toronto Research Chemicals, Canada.

Sorbent tubes Anasorb CSC (activated charcoal) and SKC tubes 226-119 (silica gel with DNPH) were purchased from SKC Inc., USA. High purity double-distilled and deionized water for dilution and all titration reagents preparation were obtained using a Milli-Q system (Millipore, USA).

Analysis of carbonyl compounds

Carbonyl compounds were analyzed based on the US Environment Protection Agency TO11 standard method for carbonyl compounds determination in air.[1] Carbonyl compounds were trapped from vapor using silica gel cartridges (150/300 mg) coated with 2,4-dinitrophenylhydrazine (DNPH). Aldehyde and ketone-DNPH derivatives were desorbed using 1 mL of acetonitrile and the solution obtained was subject to chromatographic analysis.

Carbonyl compounds were analyzed with high-performance liquid chromatography using HPLC AT 1200 system (Agilent Technologies, USA) with spectrophotometric DAD detector. Compounds were separated using Zorbax Eclipse 4.6 mm × 250 mm × 5 μm column (Agilent Technologies, USA) using gradient elution with acetonitrile/water at flow rate of 1 mL/min in controlled temperature of 40°C. Injection volume was 10 μL, total time of analysis was 25 mins, and analytical wavelength of DAD detector was 365 nm. The method allowed selective determination of the following compounds: formaldehyde, acetaldehyde, acrolein, acetone, propionic aldehyde, crotonaldehyde, butanol, benzaldehyde, isovaleric aldehyde, valeric aldehyde, m-methylbenzaldehyde, o-methylbenzaldehyde, p-methylbenzaldehyde, hexanal, 2,5-dimethylbenzaldehyde. The detection limit per one e-cigarette (150 inhalations) and their values are presented in Supplementary Table I. The calibration of the method was conducted in a range of the concentrations from 0.01 to 100 μg per one e-cigarette. The precision of the method was 18% with accuracy of 89%.

Analysis of Volatile Organic Compounds (VOCs)

The ISO 16200-1 standard of air contamination measuring was adapted for VOCs examination.[2] VOCs were trapped from vapor on activated carbon and then desorbed from

the sorbent using 1 mL of carbon disulfide (CS_2). After internal standards were added, the solution was analyzed with gas chromatography-mass spectrometry (GC-MS) using Varian 460 GC system (Varian Inc., USA) following electron ionization and SIM data collection with mass detector 320 MS (Varian Inc., USA). Compounds were separated using capillary column VF 5 MS; 30 m × 0.25 nm × 0.25 μm (Varian Inc., USA), in following temperature gradient: 40°C for 2.5 min, increased to 150°C with rate of 20°C/min, and hold for 10 mins. Injection volume was 1 μL, temperature of injector 200°C, and flow rate of carrier gas (helium) 1 mL/min. Compounds were identified by their spectra comparison with spectra included in Wiley Registry™ Library (John Wiley and Sons, Inc., USA). The method developed allowed selective determination of the following compounds: benzene, toluene, chlorobenzene, ethylbenzene, m,p-xylene, o-xylene, styrene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, naphthalene.

Based on blank sample analysis, analysis of standard and control solutions, the detection limits of compounds analyzed in samples obtained was determined. Based on these values the detection limits were calculated per one e-cigarette (150 inhalations) and their values are presented in Supplementary Table I. The calibration of the method was conducted in a range of the concentrations from 0.05 to 50 μg per one e-cigarette. The precision of the method used was 21%, and its accuracy 85%.

Analysis of Tobacco Specific Nitrosamines (TSNAs)

Currently, there is no standard method of nitrosamines determination in air, therefore the methodology used for these compounds analysis in tobacco smoke was used in the study.[3, 4] Nitrosamines from e-cigarette smoke were extracted from vapor to the liquid

phase using two gas-washing bottles with 100 mL of methanol. 20 mL of methanol solution was collected and condensed in vacuum evaporator. After condensation to 2 mL, 100 µL of solution was collected, 50 µL of internal standards (100 ng/mL) was added and mixed. We analyzed NNN and NNK using Kinetex PFP 3 mm × 150 mm × 2.6 µm column (Phenomenex, USA), in temperature of 50°C, with following mobile phase gradient flow: 20 to 80% methanol in 10 mM ammonium formate solution over 6 mins at 600 µL/min, than 100% methanol for 30 secs hold for 1 min, and re-equilibrated for 4 mins. TSNAs were analyzed using ultra performance liquid chomatography (UPLC) system Vantage Triple Stage Quad Mass Spec (Thermo Scientific, USA) with Pal Open AS and heated electrospray ionization (HESI). Following transitions were used: NNN 178>148 (retention time (RT) 2.43 min), d4-NNN 182>152 (RT 2.95 min), NNK: 208>122 (RT 3.44 min), and d4-NNK: 212>126 (RT 3.43 min).

The method developed allowed selective determination of the following compounds: N'-nitrosonornicotine (NNN) and 4-(methylnitrosamino)-1-(3-pyridyl)-1-butanone (NNK). Based on blind samples analysis, analysis of standard and control solutions, the detection limits of compounds analyzed in samples obtained was determined. Based on these values the detection limits were calculated per one e-cigarette (150 inhalations) and their values are presented in Supplementary Table 1. The calibration of the method was conducted in a range of the concentrations from 0.1 to 50 ng per one e-cigarette. The precision of the method used was 19%, and its accuracy 87%.

Analysis of metals

Metals were planned to be analyzed in a similar methods like previously applied for tobacco smoke analysis.[5, 6] Metals were extracted from vapor to the solid phase which was methanol. 10 mL of methanol solution was collected, and condensed on vacuum evaporator. The samples were acidified with 0.5 mL of 70% nitric acid and heated at a temperature of 120ºC for 8h. Then 10 mL of deionized water and 10 ng/mL rhodium (Rh) as an internal standard was added and samples were subjected to analysis.

All solutions of multielemental (Merck, Germany) and monoelemental standards were prepared daily by the dissolution reference materials (Merck, Germany) in water obtained from Milli-Q System (Millipore, USA) and used for the calibration. Standards, blanks and samples were measured using the same internal standard (10 ng/mL Rh). Solution of 10 ng/mL Rh was move into all solutions on line, by second tubing on peristaltic pomp. Ultrapure concentrated nitric acid was used for adjusting samples and standard solutions acidity.

Selected trace-elements were analyzed using the inductively coupled plasma mass spectrometry technique (ICP-MS). The Sciex ELAN 6100 DRC-e quadruple spectrometer (Perkin-Elmer, USA) was used. The system was equipped with Cetax 500 autosampler and a cross flow nebulizer (Cetax, USA). The spectrometer was optimized to provide maximal intensity for ^{24}Mg, ^{115}In, ^{238}U, and minimal values for CeO/Ce (below 3%) and Ba^{2+}/Ba (below 3%). The optimum measurement conditions were as follows: Rf power 1025 W, plasma gas flow 15 L/min, nebulizer gas flow of 0.70-0.76 L/min, auxiliary gas flow of 1.13 L/min, cross flow nebulizer, quartz plasma torch, nickel skimmer and sampler cone, sample uptake of 1 mL/min, peak hop scanning mode, dwell time of 100 msec, 20 sweeps/reading, number of replicates 3, and read delay time of 15 sec.

The 1643e NIST (National Institute of Standards and Technology, USA) reference material was used to verify the quality of the measurements. Certified values of concentration

from this reference material are available for all analyzed elements in this work. The determined values agreed well with these certified values. The method developed allows to determine the following elements: cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), selenium (Se), manganese (Mn), barium (Ba), rubidium (Rb), strontium (Sr), silver (Ag), thallium (Tl) and vanadium (V). Based on blind samples analysis, analysis of standard and control solutions, the detection limits of compounds analyzed in samples obtained was determined. The detection and quantification limits of analyzed elements were below 0.01 μg for all analyzed metals and are presented in Supplementary Table 1. The calibration of the method was conducted in a range of the concentrations from 0.01 to 20 μg per one e-cigarette (150 puffs). The average precision of the method used was 23%, and its average accuracy 84%.

REFERENCES FOR SUPPLEMENTARY MATERIALS

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